SYNTHESIS OF THE COMPLEX OF CHLORODIPHENYLBORANE WITH DIMETHYLFORMAMIDE

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Great importance has recently been acquired by organic complex compounds used as intermediate products or as catalysts in various reactions. The molecules forming constituents of the complex must be fairly labile and reactive. Thus, when reactions are carried out with organoboron acid halides (used in the form of their complexes with amides), those complexes are preferred in which the electron acceptors (Lewis acids) are acid chlorides or bromides (and to a less extent fluorides) and the electron donors (Lewis bases) are tertiary amides.

For the esterification of polyvinyl alcohol with organoboron acid chlorides, which we carried out for the first time [1], it was shown that electron-donating polar solvents—pyridine and dimethylformamide—are the most suitable solvents to bring about this reaction. It was shown at the same time that chlorodiphenylborane forms complex compounds (adducts) both with pyridine and with dimethylformamide. Dimethylformamide has a high dielectric constant ($\varepsilon = 37$), but in determining the effect of the medium on the course of the reaction we must always take account not only of the polarity of the solvent, but also its power of complex-formation. The high solubility of many Lewis acids (including many organoboron compounds) in amides indicates that both the basicity, which determines the power of complex-formation, and the dielectric constant, are important factors for the understanding of the action of the solvent and for the choice of the best solvents. The high solvent power of dimethylformamide has attracted the attention of a number of investigators, but the mechanism of its action as a solvent has still been studied little.

The complex-forming properties of amides, including dimethylformamide, have been described previously. Amides form complexes with the hydrogen ion [2] and with the metal ions of some inorganic chlorides (Cu, Cd, Hg, Ti, Co, Ni, Sb, Sn, Mn). Complexes of amides with mercuric bromide, iodine, bromine, SO$_3$, thionyl chloride, PBr$_5$, POBr$_3$, POCl$_3$, and COCl$_2$ have also been described. Amides are able to form complexes also with molecules of electron acceptors of the Lewis type, e.g., with boron trihalides (complex of dimethylformamide with BF$_3$) [3]. As regards the derivatives of organoboron compounds with amides, only the derivatives of tetraphenylboron with dimethylformamide and other amides have been described [4]. For more details about amide complexes see the review [5].

A study of the complex-forming power of diarylchloroboranes, in particular chlorodiphenylborane, shows that chlorodiphenylborane is a stronger Lewis acid than other organoboron compounds, e.g., trialkylboranes. Chlorodiphenylborane is able to form solid 1:1 complex compounds with amides, for example, ammonia, pyridine, 2,6-lutidine, and quinoline. Complex compounds of chlorodiphenylborane with two molecules of primary amides have also been described. The only complex of chlorodiphenylborane with an oxygen-containing compound that has been described is the complex with p-dioxane.

**EXPERIMENTAL †**

Preparation of Chlorodiphenylborane. Chlorodiphenylborane was prepared from boric acid in accordance with the scheme:

$$B(OH)_3 \rightarrow B(OC_6H_5)_3 \rightarrow (C_6H_5)_2BOC_6H_5 \rightarrow (C_6H_5)_2BCl$$

*Deceased.
†All operations were carried out in an atmosphere of pure dry nitrogen.
Triisobutyl Borate was prepared by Bannister's method [6] in 95% yield under the conditions used for the preparation of tributyl borate; b. p. 83-85° (8 mm) \(d_4^{20} 0.8389\); \(n_D^{20} 1.4035\); found MR 67.0; calculated MR 66.40. The literature gives: b. p. 84-86° (10 mm); \(d_4^{20} 0.8390; n_D^{20} 1.4035\).

Isobutyl Diphenylborinate. Contrary to the views of Klages, who considered that in the reaction of organomagnesium compounds with trialkyl borates only boronic esters are formed, experiments showed that even with a molar ratio of reactants of 1:1 in addition to areneboronic esters also diarylborinic esters are formed. In the reaction of two equivalents of phenylmagnesium bromide with one of tributyl borate, butyl diphenylborinate is obtained together with the benzeneboronic ester and triphenylborane [7].

\[
2C_8H_{19}MgBr + B(OC_8H_{19})_3 \rightarrow (C_8H_{19})_2BOC_8H_{19} + 2Mg(OC_8H_{19})Br
\]

In the reaction mechanism suggested, a tetracoordination complex (anion) is formed in the first stage in accordance with the scheme:

\[
C_8H_{19}MgBr + B(OC_8H_{19})_3 \rightarrow [(C_8H_{19})_2B(OC_8H_{19})_2]^{-}MgBr^+ \xrightarrow{3H_2O} C_8H_{19}B(OH)_2 + 3i-C_4H_9OH + Mg(OH)Br
\]

The diphenylborinic ester is formed by the reaction of the benzeneboronic ester with phenylmagnesium bromide:

\[
(C_6H_5)_2BOC_8H_{19} + C_6H_5MgBr \rightarrow (C_6H_5)_2B(OC_8H_{19}) + MgBr
\]

All authors considered that it was impossible to isolate butyl diphenylborinate from the reaction mixture. It was supposed that when the reaction mixture is treated with dilute acid, the free diphenylborinic and benzeneboronic acids are obtained. However, Mikhailov and co-workers [8] in a study of the action of arylmagnesium bromides on triisobutyl borate showed that isobutyl diarylborinates can be isolated from the reaction mixtures in good yields and that these, unlike areneboronic esters, are stable to the action of dilute acids and are not hydrolyzed under these conditions. We prepared isobutyl diphenylborinate by the reaction of two equivalents of phenylmagnesium bromide with one of triisobutyl borate by the method of Mikhailov and co-workers [8] in 57% yield. The substance had: b. p. 152-155° (8 mm); \(d_4^{20} 0.9767; n_D^{20} 1.5393\); found: MR 76.24; calculated; MR 76.65. The literature gives: b. p. 152-154° (8 mm); \(d_4^{20} 0.9768; n_D^{20} 1.5432\).

Chlorodiphenylborane, Mikhailov and co-workers obtained chlorodiphenylborane (diphenylborinic chloride) by the action of phosphorus pentachloride on propyl diphenylborinate [9]. We prepared chlorodiphenylborane by the same method, but by the action of phosphorus pentachloride on isobutyl diphenylborinate:

\[
(C_6H_{19})_2BOC_8H_{19} + PCl_5 \rightarrow (C_6H_{19})_2BCl + POCl_3 + i-C_4H_9Cl
\]

The substance had: b. p. 119-120° (3 mm); \(d_4^{20} 1.1091; n_D^{20} 1.6075\); found MR 62.48; calculated MR 61.65. The literature gives: b. p. 119-120° (3 mm); \(d_4^{20} 1.1160; n_D^{20} 1.6091\).

Dimethylformamide was purified by shaking it with solid KOH and then with lime, after which it was distilled at atmospheric pressure. The fraction coming over at 152-153° was cooled and then vacuum-distilled at 10 mm.

Solvents: methylene chloride was purified by shaking it with P₂O₅ and distilled, and petroleum ether, pentane, and diethyl ether were dried by the usual methods.

Preparation of the Complex of Chlorodiphenylborane with Dimethylformamide \((C_6H_{19})_2BCl \cdot HCON\left(CH_3\right)_2\). The formation of the complex of chlorodiphenylborane with dimethylformamide was brought about by shaking or mechanically stirring a mixture of the reactants. The complex was obtained either as a solution in an inert solvent (methylene chloride), from which the reaction product was isolated by driving off the solvent in a vacuum, or as a precipitate in the precipitant as medium (petroleum ether, pentane, or diethyl ether). The complex was obtained also in dimethylformamide solution and used directly in the esterification of polyvinyl alcohol.